CARS DETECTION OF GASEOUS SPECIES FOR DIAMOND DEPOSITION PROCESS

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ABSTRACT

In order to understand the complicated chemical and physical processes that occur during the deposition of hard face coatings such as diamond, diagnostics that are remote, nonintrusive and sensitive to potential chemical species are necessary. One particularly promising approach is coherent anti–Stokes Raman spectroscopy (CARS) useful for measurements of temperature and species concentrations. Results to be described will include CARS measurements on a PACVD reactor used for depositing high quality diamond films. A mixture of acetylene (C_2H_2) and Argon, tested over a range of total pressures down to 0.1 Torr, was used to calibrate the CARS system. With the existing CARS system, detectivity of C_2H_2 to 5 mtorr was demonstrated. This paper describes details of the scanned narrowband colinear CARS system and examples of CARS spectra obtained for CH_4 and C_2H_2 species under rf PACVD diamond deposition conditions and also using an alternate filament–assisted technique.

INTRODUCTION

Nonequilibrium reactive plasmas are recognized as a novel approach for a wide variety of material coating applications (1). This type of plasma provides a unique environment wherein deposition of thin, hard face, conformal coatings can occur at much lower temperatures (critical for inhibiting stresses) and within more complex chemical environments than are possible by conventional vapor deposition techniques. A need exists for in–situ nonintrusive techniques for diagnosing and controlling PACVD systems used for thin coating deposition (2). If improvements can be made in durable hard face coatings, increased utilization of lightweight materials under advanced development may follow. A complete understanding of the process requires information on a large number of physical and chemical processes involving gas phase and gas–surface interactions and the associated synergistic effects. Knowledge of plasma species concentrations and "temperature" is required for correlation with the corresponding physical and chemical properties of the coatings.

Emission spectroscopy is often used for the measurement of atomic and molecular species, but the emission from excited atomic levels is often much larger than for excited molecular levels, thus the atomic species dominate the spectra and molecular signatures are difficult to extract. Species concentration is difficult to infer from plasma emission spectra because they involve excited electronic levels that are not generally in thermodynamic equilibrium with the ground state. An alternative diagnostic technique, sensitive to the molecular ground state, is Coherent Anti–Stokes Raman Spectroscopy (CARS), a nonlinear optical technique useful for measuring the concentration and "temperature" of molecular constituents since all molecules have at least one Raman active vibrational mode.

The outstanding combination of unique material properties of diamond offers the potential for applying diamond coatings in many commercial applications ranging from protective and tribological coatings to films/ heat sinks for semiconductors to optical lenses to electronic devices for space environments. Before diamond coatings can be applied to commercial type applications, many questions need to be answered.

Ti–6A1–4V was selected as the reference substrate material. It represents a critical alloy of paramount interest in many commercial/aerospace applications. Its strength to weight and low temperature oxidation/ corrosion resistance are excellent. However, erosion and wear occur rapidly, thus the need for durable hard face coatings.

APPARATUS

Figure 1 is a schematic of the nonequilibrium PACVD reactor under current investigation at UTRC. The longitudinal, tube type radio frequency (rf) geometry was selected as a design viable for later scale up to continuous production operation. In addition it permits high reactant gas flows and plasma power levels; increasing these parameters nominally results in enhanced deposition rates. The 3.6-cm-ID test section is constructed of high purity fused silica and high vacuum flanges for rapid disassembly. Up to 5 different reactant gases can be simultaneously injected at the inlet region. A 5 kW rf power supply operating at 13.56 MHz is used to inductively couple the rf power into the plasma through a multiple-turn water-cooled copper work coil. Exploratory test results revealed the importance of minimizing contamination in the PACVD system as required for providing high quality coatings onto the 1.3-cm-dia x 2-mm-thick Ti-6A1-4V substrates. As a result, a completely oil-free, venturi, vacsorb, cryopump and vacion pump system are used, including a MKS flow metering system with special traps (e.g., GaInAl) and getters to remove water vapor and oxygen. To augment pumpdown time and provide operating range flexibility, a 380 ℓ/s turbomolecular pumping system, modified for corrosion resistant operation, is used; a residual gas analyzer to monitor trace impurities is also used. This system is capable of initial operating pressures down to 10^{-7} torr. The cleanliness of the substrate prior to coating deposition is believed to be a key requirement for achieving good coating adherence to the substrate. Therefore, a test sample holder and isolated load-lock and transport system are interfaced with the PACVD system (3). This technique allows direct Secondary Ion Mass Spectrometry/Ion Scattering Spectrometry (SIMS/ISS) analysis of the substrates immediately following in-situ plasma cleaning and provides a unique capability not reported in the literature. Additional advantages of this type system include the provision for conformal coverage for complex shapes, graded composition control, and provision for independent biasing and temperature monitoring of the substrate.

As hardness and adhesion are critical parameters for characterizing thin, hard face coatings, a state-of-the-art ultramicrohardness tester and UTRC custom built adhesion test apparatus have been installed and preliminary calibration testing initiated. The ultramicrohardness tester (Nanoindenter) can resolve forces as small as 2.5μN and displacements of 0.4 nm. The adherences measurements are made on a computer-controlled pin-on-disc apparatus that has a 3-axis force transducer and a device to measure the advance of the pin into the coating. A modification to this device using an ultrasonic sensor allows for coating delamination detection. Reference 3 describes details of this equipment and initial test results.

DIAGNOSTICS

The theory of CARS is explained in several recent reviews (4,5). Figure 2 is a simplified schematic of the colinear phase-matched CARS system used in these experiments. As illustrated in Figure 2, incident laser beams at frequencies ω_1 and ω_2, termed the pump and Stokes respectively, where $\omega_1 > \omega_2$, interact through the third-order, nonlinear susceptibility of the medium to generate the coherent CARS radiation at frequency $\omega_3 = 2\omega_1 - \omega_2$. The frequency difference $\omega_1 - \omega_2$ is adjusted to access the Raman-active vibrational-rotational resonances in a given constituent. Since the characteristic vibrational frequencies of most molecules are well separated, individual species are easily addressed. The CARS process must be phase matched so that the developing signal grows constructively. The scanned, narrowband CARS approach, rather than a broadband approach, was selected due to its very high spectral resolution and maximum species detectivity. It is best used to study temporally-steady processes such as PACVD, but it has the disadvantage of being quite time consuming. Species measurements can be made from the absolute signal strength. In addition to the resonant signal from the Raman modes of interest, there is also a nonresonant electronic background contribution from all the molecules or atoms present in the control volume. This leads, due to destructive interference effects in the coherent wave mixing, to spectral signatures which are also concentration sensitive. Thus fractional concentrations can be obtained from spectral shapes without regard to signal level fluctuations caused by beam steering or particle attenuation.

As shown in Figure 2, the dye laser is scanned to generate the CARS spectrum. In this way all of the available laser pump energy excites a single transition of the resonant molecule and increases the sensitivity

by several orders of magnitude. For equivalent laser powers, decreasing the Stokes bandwidth from the typical broadband value of 150 cm^{-1} increases the CARS signal by over 10^3 due to the increased spectral intensity. Spectral scanning from 60–100 cm^{-1} requires about 30 minutes.

The basic equipment includes an injection–seeded, single–mode, Nd:YAG primary beam pump laser which is frequency doubled to produce narrow bandwidth ($\sim$ 50 MHz), 10^{-8} sec pulses at 532 nm at a 10 Hz repetition rate and a narrow bandwidth (0.4 cm^{-1}) scanned Stokes dye laser. A major portion of the primary beam is split off to drive the dye laser. The remaining 532 nm beam serves as the pump and is combined colinearly with the Stokes beam at a dichroic prior to focussing in the plasma test region. The frequency–shifted CARS signal is formed in the laser focus and all three beams exit the reactor where a dichroic separates the CARS from the incident wave mixing beams. Digital acquisition of the CARS and reference signals are obtained from fast, gated PMT detectors. The digital acquisition system also records the wavelength shift of the scanned dye laser for calibration of the CARS spectrum. All signals from the PMT are digitized on every pulse and processed in a computer. As the dye laser is scanned, successive transitions of the molecular resonances are excited and modulate the intensity of the CARS signal. The result is a spectrum of the ro-vibrational manifold of the medium from which identification of species, their concentration and temperature (vibrational and rotational) can be obtained. Typically, ten CARS pulses are averaged per spectral step which corresponds to 0.1 cm^{-1}. With appropriate referencing, the molecular concentration can be measured to within $\pm 1\%$ of the total gas density and the population in the vibrational and rotational states determined for assignment of temperatures.

RESULTS TO DATE AND DISCUSSION

In the exploratory experiments directed at diamond coatings, a mixture of 1% CH_4 in H_2 was used at a total pressure of 5 torr. The rf coils were located at the optical port location. Figure 3 is an example of the CARS methane signal obtained for the ν_1 mode. It illustrates the effect of increasing rf power from zero up to 400 Watts on depleting the methane concentration. Measurements were also made of the weaker 2 ν_2 and ν_3 modes as shown in Figure 4.

Very little is known about the chemical mechanisms of diamond film growth. Several global kinetic theories have been proposed based on nucleation theory and equilibrium. Other proposed mechanisms rely on the presence of C_2H_2 or CH_3^+. Spear and Frenklach at Pennsylvania State University (6) have proposed an alternative mechanism for diamond growth. It basically consists of two alternating steps. First, the surface is activated by H–atom removal of a surface–bonded hydrogen. The surface activated carbon radical then acts as a site for adding more carbons to the structure by reacting with acetylene (C_2H_2) in the plasma. To provide more quantitative experimental information to verify these proposed theories and improve the basic understanding of the diamond growth process, a series of CARS experiments was conducted focused on measurement of the C_2H_2 molecular species. C_2H_2 is a linear molecule with five fundamental vibrations. Three of the five modes are Raman active. Figure 5 displays a scan generated CARS spectrum of 5% C_2H_2 in an Ar background (ν_1 band) measured using the CARS system shown in Figure 2. This measurement was made at room temperature and 10 torr reactor total pressure while flowing the mixture of 5% C_2H_2 in Argon. High purity C_2H_2, as checked via a gas chromatograph, in concentrations of both 5% and 0.5% in Argon were used in these measurements. The measurements obtained using both concentrations indicate a C_2H_2 detectability of 5 mtorr was achieved with the present system. Continued improvements in spectral filtering should significantly improve its sensitivity level.

To determine the effect of rf plasma location on the ability to detect the C_2H_2, a series of tests was conducted for the different configurations shown in Figure 6. In each case the total pressure was 3 torr. The 5% C_2H_2 in Argon was only detected when the rf plasma was located downstream of the laser optical ports. In the other locations, the concentration of C_2H_2 was less than 5 mtorr. The next step was to investigate the configuration and test parameters under which high quality diamond coatings have been deposited. The results for the CARS spectrum of C_2H_2, ν_1 mode observed at 3 torr, is shown in Figure 7. The rf power input

to the plasma was 300 watts and the H_2 and CH_4 flow rates were 99 and 1 sccm respectively. The rf coils were located at the optical port axis and the Ti-6A1-4V substrate was located within the plasma plume and 1-cm downstream of the optical centerline. Additional experiments have also included measurements with the substrate located approximately 1 mm from the laser beam. No significant C_2H_2 CARS signal was observed in any of these tests. This would indicate, if C_2H_2 were present, that it was at concentration levels less than the 5 mtorr current detection limit of the CARS system.

To apply this CARS technique to other diamond deposition systems, a hot filament reactor configuration, similar to that reported by Celii, et al. (7) was fabricated and measurements were made of the C_2H_2 CARS spectrum. Figure 8 is a schematic of the test geometry. The gas flow was 1% CH_4 in H_2 at a pressure of 150 Torr and maintained at 200 sccm. A 2-mm-dia. x 2-cm-long tungsten filament heated to approximately 2630K was located 2 cm from the Ti-6A1-4V substrate. Figure 9 shows the scan generated CARS spectrum of the C_2H_2 ν_1 band, thus verifying the presence of C_2H_2 close to the surface of the substrate as reported by Celii, et al.

Figure 10 is an example of the test results obtained using Raman scattering on a Ti-6A1-4V substrate that was coated with the polycrystalline diamond film using the rf PACVD process. In these measurements, a tunable cw dye laser operated in a single frequency configuration with a line width of < 5 MHz, tuned to 16956.18 cm^{-1}, was used as the excitation source. Raman spectra reported by Matsumoto (8) for thin diamond films indicate only one sharp peak at about 1333 cm^{-1}. This is very close to the value 1332.5 cm^{-1} reported for natural diamond by Solin and Ramdas (9). A feature of the UTRC diamond coating obtained via rf PACVD is that no graphite peak was detected in any of the Raman measurements. X-ray diffraction measurements indicated the observed interplanar spacings are in close agreement with reported values (2.065 and 1.262 Å) of natural diamond (ASTM 6-675) and UTRC reference natural diamond material.

Based on the above experiments, the following are the preliminary results: 1) a CH_4 CARS spectrum was observed in the rf plasma, 2) increasing the rf plasma power reduced the CH_4 CARS signal, 3) the rf plasma significantly reduces the C_2H_2 CARS signal in C_2H_2/Ar flow, 4) the C_2H_2 CARS spectrum was not observed in rf plasma CH_4/H_4 diamond deposition tests to date. The present C_2H_2 detectability limit is 5 mtorr, and 5) the C_2H_2 CARS spectrum was observed in the hot filament reactor configuration.

SUMMARY

Laser/optical diagnostic techniques, such as the CARS system described in this paper, are candidates for application as plasma gas phase materials processing diagnostic tools, each with its own inherent advantages and associated limitations. Recognizing that no one diagnostic technique will suffice, it will only be through the complementary use of several of these techniques that a fundamental understanding of the relationship between plasma process variables and properties of the processed material coating will evolve. This may ultimately lead to simple process control strategies, including in-situ laser diagnostics and sensors, to ensure high quality, economic, reproducible plasma deposition of advanced coatings such as diamond in a production scale environment. Research addressing these aspects is continuing.

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(8) Matsumoto, S., Y., Kamo, M., Tenaka, J., and Setaka, N., *Chemical Vapor Deposition of Diamond from Methone–Hydrogen Gas*, Proc. 7th International Conference on Vac. Metallurgy, pp. 386–391, Tokyo, Japan, 1982.

(9) Solin, S., and Ramdas, A., *Raman Spectrum of Diamond*, Phys. Rev. B1, pp. 1687–1698, 1970.
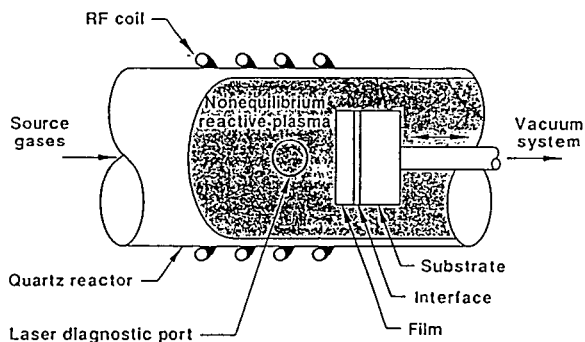
FIGURE 1.   SCHEMATIC OF PACVD REACTOR USED
FOR DIAMOND DEPOSITION EXPERIMENTS .
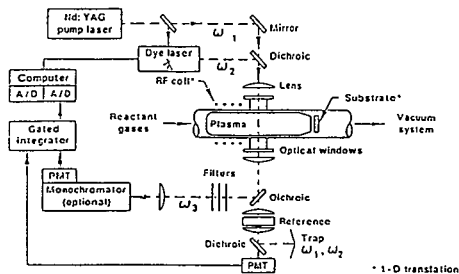
FIGURE 2. SCHEMATIC OF NARROWBAND, COLINEAR
SCANNED CARS SYSTEM USED IN PACVD
DIAMOND FILM DEPOSITION
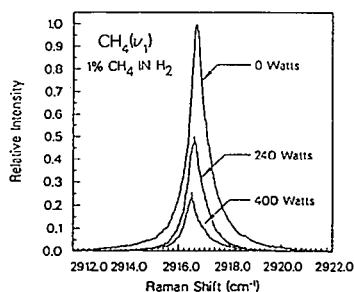
FIGURE 3. EFFECT OF RF PLASMA POWER
ON CARS METHANE SPECTRUM
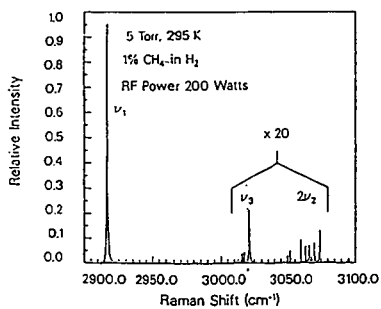
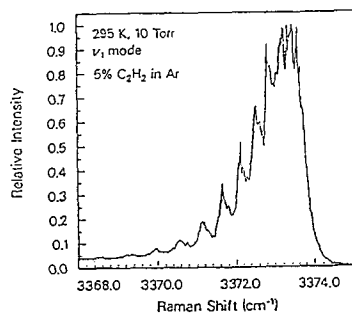FIGURE 4. CARS METHANE SPECTRUM
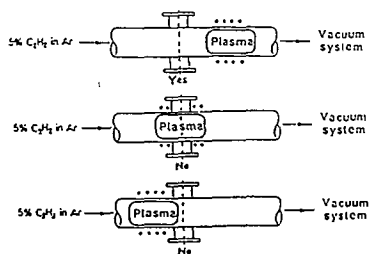OF DIFFERENT MODES

FIGURE 5. CARS SPECTRUM OF ACETYLENE
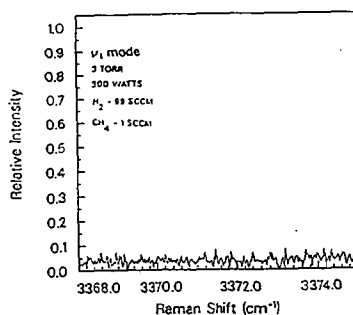

FIGURE 6. C$_2$H$_2$ DETECTION LOCATIONS

FIGURE 7. CARS SPECTRUM OF ACETYLENE IN PACVD
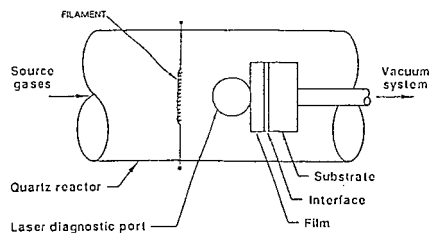DIAMOND COATING DEPOSITION

FIGURE 8. SCHEMATIC OF HOT FILAMENT
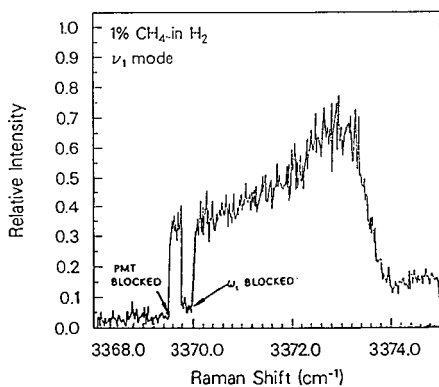REACTOR CONFIGURATION

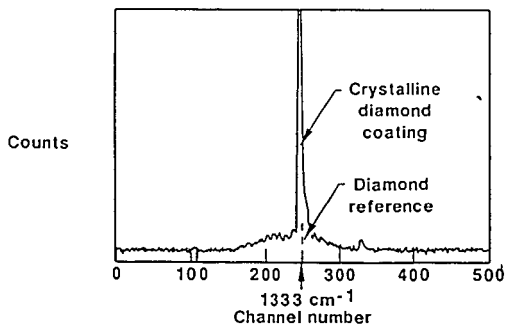FIGURE 9. CARS SPECTRUM OF ACETYLENE
IN HOT FILAMENT CONFIGURATION

FIGURE 10. RAMAN SPECTRA OF DIAMOND COATING
DEPOSITED VIA PACVD ON Ti-6Al-4V SUBSTRATE.